Towards the Marine Biorefinery: Seawater Fractionation of Macroalgae.

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Why seawater?

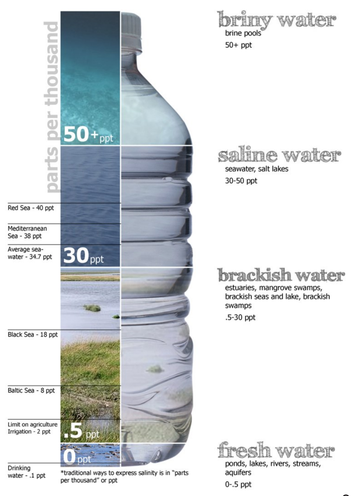
- The **Marine Biorefinery** concept is built on seaweed and algae
- **Seaweed** is wild-harvest from the oceans, it's a better resource than terrestrial biomass crops in many ways[1]
- Oceans are **saline**, 35 parts per thousand of salt on average
- Current Marine Biorefinery research takes place in the Lab in **Freshwater**
- Why not just do the basic chemistry **directly in seawater?**

Experimental Questions:

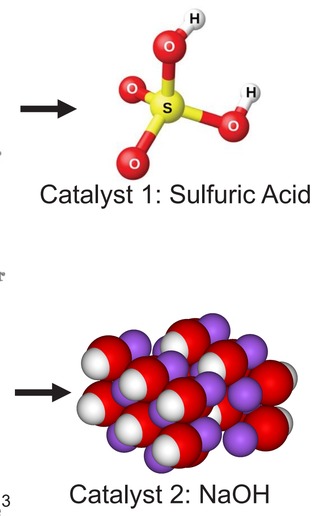
- How does the presence of salt impact a simple model fractionation reaction?
- Does the presence of salt influence the optimal reaction conditions?
- Does the presence of salt inhibit a model fermentation organism?

Materials

Macroalgae: *Fucus serratus*[2]



Solvent: Freshwater to Brine[3]

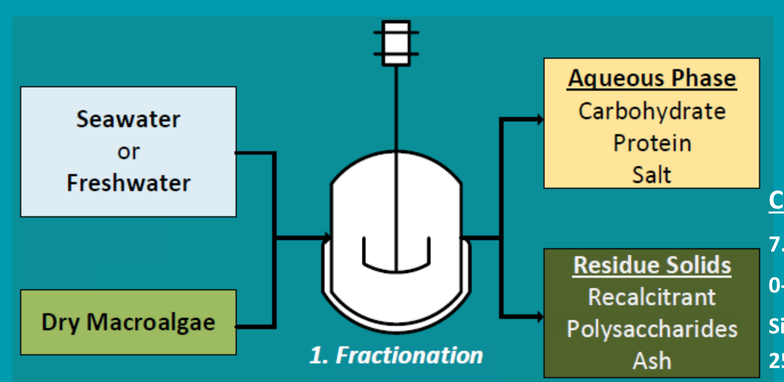


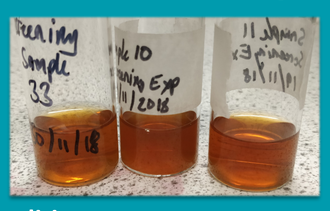
Catalyst 1: Sulfuric Acid

Catalyst 2: NaOH

1. Fractionation:

- ✓ **Design of Experiment: Multifactorial screening experiment, varying salinity, reaction temperature, and choice of catalyst**
  - ✓ **HPLC for sugars, gravimetry for yields. CHN on solids, TOC on Aq.**





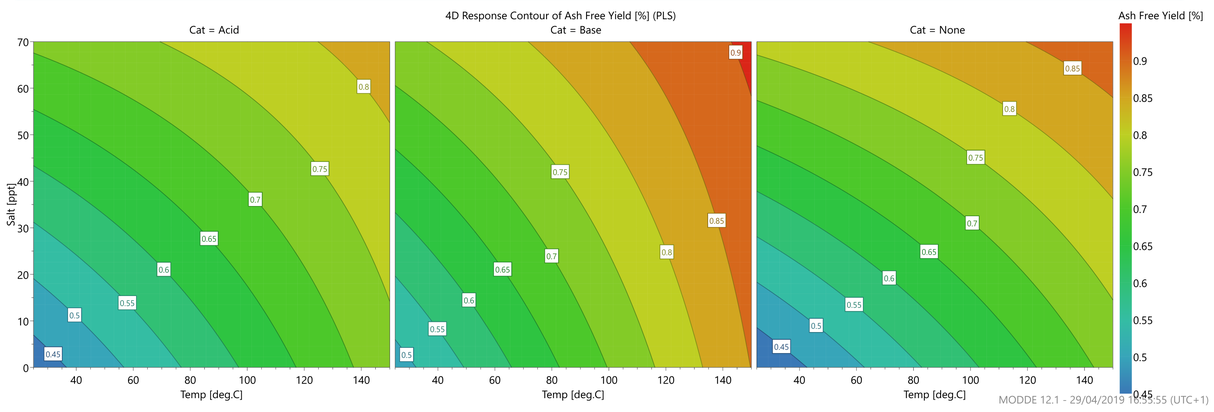
Conditions:

7.5 wt. % NaOH or 2.0% v/v H_2SO_4

0-70 ppt salt-water solvent (10 mL)

Simple fractionation (20 min stirred, 25 to 150°C, 5 % wt. solids loading)

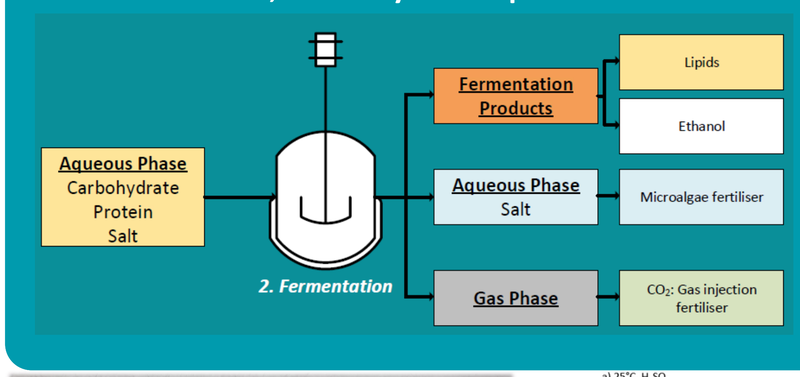
Separation by centrifuge



4D response plot: *Ash-free solids conversion yield as a function of reaction temperature, catalyst choice, and solvent salinity. Optimal conversion yield found at high temperature, with NaOH, and seawater*

2. Fermentation[4]:

- ✓ **96-Well Plate format for rapid screening of experimental space**
- ✓ **OD_{600} absorption every 30 minutes for 5.5 days**
- ✓ ***Metschnikowia pulcherrima* (NCYC 4331) - inhibitor tolerant, catabolises oligo-saccharides, makes synthetic palm oil[4]**

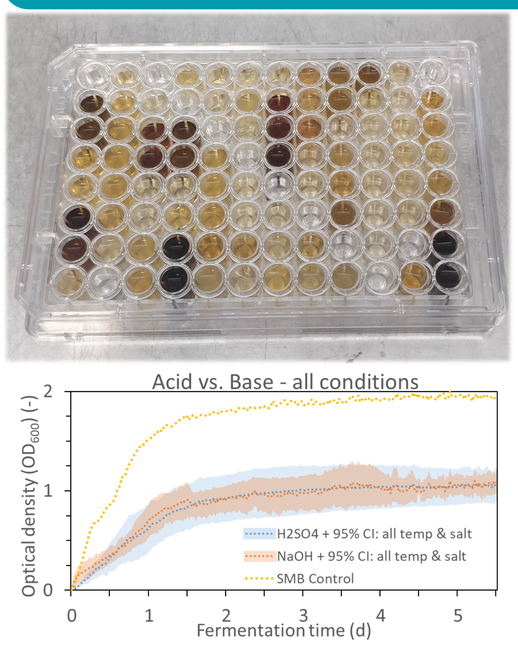


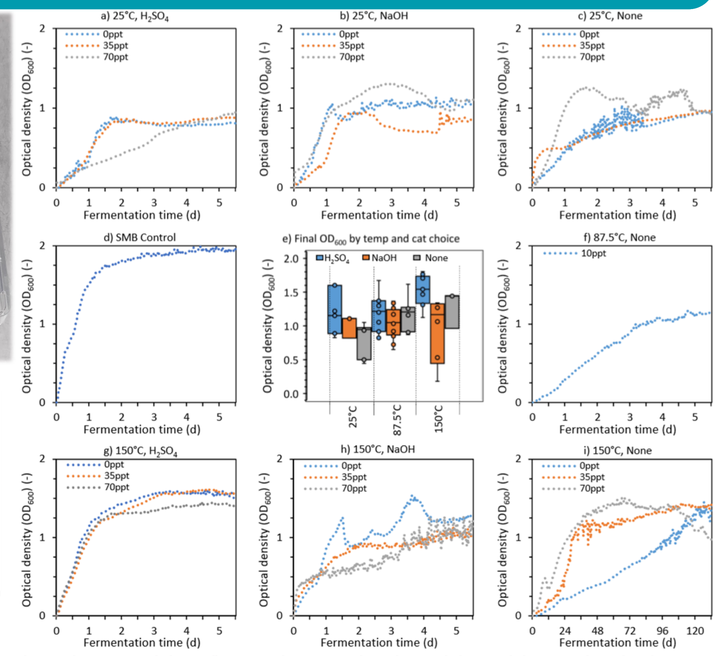
Conditions:

2.5% vol. inoculum, 300 µL working volume

12 mg/L tetracycline, 15 mg/L gentamicin.

Incubation at 25°C, orbital shaking 200rpm

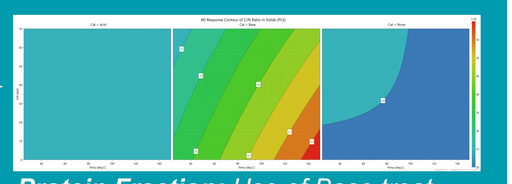




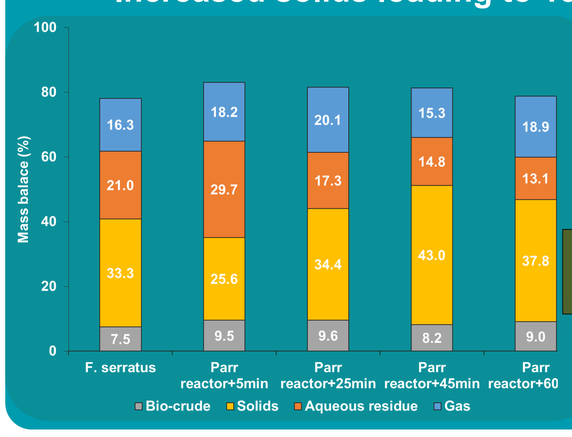
Rapid fermentation screening: *M. pulcherrima is capable of growing on both acid and base hydrolysates, and at all salt concentrations. Base conditions make for simpler reactor design due to materials of construction compatibility.*

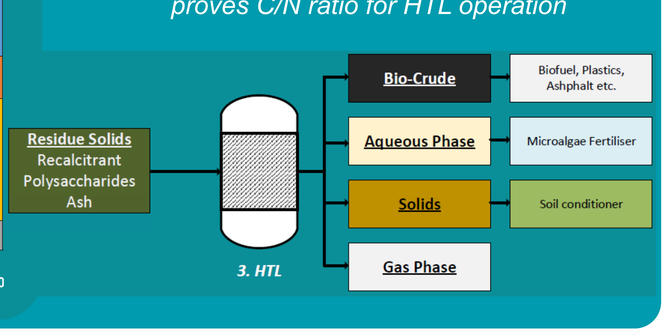
3. Hydrothermal Liquefaction[5]:

- ✓ **Run on Base hydrolysate solids only**
- ✓ **Increased solids loading to 13 % wt.**



Protein Fraction: *Use of Base treatment directs Nitrogen to Aq. Phase, improves C/N ratio for HTL operation*





Conclusions:

- ♦ **NaOH treatment improves HTL products, and no disadvantage vs. H_2SO_4 digestion**
- ♦ **Seawater (35ppt) vs freshwater has negligible effect on fractionation & fermentation**
- ♦ **HTL vs. Fermentation products can be directed by simple temperature control**

References:

1. K. A. Jung, S. R. Lim, Y. Kim and J. M. Park, *Bioresour. Technol.,* 2013, **135**, 182–190.
2. "Fucus serratus2" by Stemonitis (https://commons.wikimedia.org/wiki/File:Fucus_serratus2.jpg) accessed 30-Apr-2019, shared under Creative Commons Attribution-Share Alike 2.5 https://creativecommons.org/licenses/by-sa/2.5/legalcode
3. "Water salinity diagram" by Peter Summerlin (https://commons.wikimedia.org/wiki/File:Water_salinity_diagram.png) accessed 30-Apr-2019, shared under Creative
4. F. Abeln, J. Fan, V. L. Budarin, H. Briers, S. Parsons, M. J. Allen, D. A. Henk, J. Clark and C. J. Chuck, *Algal Res.,* 2019, **38**, 101411.
5. S. Raikova, T. D. J. Knowles, M. J. Allen and C. J. Chuck, *ACS Sustain. Chem. Eng.,* 2019, **7**, 6769–6781.

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